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# Behavior of Alkali Metals in the Hydrogen Flame Ionization Detector for Ultra-Micro Analysis of Alkali and Alkaline Earth Metals

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Behavior of alkali metals in the small hydrogen flame for ultra-micro analysis of alkali and alkaline earth metals were investigated. Distribution of free neutral atoms and formation of alkali hydroxides were studied by the photometric method, distribution of charged particles was determined by the Langmuir probe method, and confirmation of whether negative-charged particles are mostly electrons or negative ions by the sheath method. It was found that only lithium formed hydroxide in the flame, ionization chiefly occurred in the part 0—5 mm above the jet, and that most of negative-charged particles are not electrons but negative ions.

A new method for ultra-micro analysis of alkali and alkaline earth metals was developed by the authors,[1-3] a hydrogen flame ionization detector being used as a sensor. The detector, in which the electric current caused by ionization of the metal in flame is measured, has high sensitivity (*e.g.*, $10^{-14}$ mol in Rb and Cs).

Since the ionization method is based on the ionization of alkali and alkaline earth metals, it is important to investigate the behavior of the metals in flame. Physical investigations[4-10] have been carried out on ionization mechanisms or kinetics of alkali and alkaline earth metals in flame. Positive ion and electron concentrations were measured by the Langmuir probe method[4] and high-frequency method,[5-10] respectively. The former has been used for determining positive ion concentration in hydrocarbon flames.[11-14]

1) S. Araki, S. Suzuki, and T. Hobo, *Bunseki Kagaku*, **15**, 27 (1966).
2) S. Araki, S. Suzuki, T. Hobo, T. Yoshida, K. Yoshizaki, and M. Yamada, *ibid.*, **17**, 847 (1968).
3) S. Araki, S. Suzuki, T. Hobo, and M. Yamada, *ibid.*, **19**, 493 (1970).
4) H. F. Calcote and I. R. King, Fifth Symposium (International) on Combustion, Reinhold, New York (1955), p. 423.
5) F. M. Page and T. M. Sugden, *Trans. Faraday Soc.*, **53**, 1092 (1957).
6) P. F. Knewstubb and T. M. Sugden, *ibid.*, **54**, 372 (1958).
7) P. J. Padley, F. M. Page, and T. M. Sugden, *ibid.*, **57**, 1552 (1961).
8) P. J. Padley and T. M. Sugden, Eighth Symposium (International) on Combustion, Williams & Wilkins, Baltimore (1962), p. 164.
9) K. Schofield and T. M. Sugden, Tenth Symposium (International) on Combustion, Academic Press, New York (1965), p. 589.
10) A. N. Hayhurst and T. M. Sugden, *Trans. Faraday Soc.*, **63**, 1375 (1967).
11) I. R. King, *J. Chem. Phys.*, **37**, 74 (1962).
12) H. F. Calcote, Eighth Symposium (International) on Combustion, Williams & Wilkins, Baltimore (1962), p. 184.
13) H. F. Calcote, Ninth Symposium (International) on Combustion, Academic Press, New York (1963), p. 622.
14) G. Wortberg, Tenth Symposium (International) on Combustion, Academic Press, New York (1965), p. 651.

Most flames were pre-mixed flames whose temperature distributions were attained only in vertical direction, and were much larger (burner mouth several centimeters in diameter) than the diffusion flame used in this experiment. Metallic elements were added to the inner flame as fine sprays of dilute aqueous solution.

Behavior of alkali metals in a small diffusion flame were studied when alkali chlorides were added to the outer flame as vapor. Distribution of free neutral atoms and charged particles, and mobility of charged particles were determined by the flame photometric method, Langmuir probe method, and sheath method,[15] respectively. The results are discussed.

## Experimental

The hydrogen flame ionization detector was the same type as that used previously.[3] The inner diameters of the evaporating and ionizing jets were 0.6 and 1 mm, respectively. The flow rates of hydrogen and oxygen for the ionizing flame (the upper flame) were 240 and 25 ml/min, respectively, and for the vaporating flame 120 and 85 ml/min, respectively. Alkali metals were continuously supplied to the ionizing flame by the evaporation of chlorides of alkali metals. A spiral of platinum wire (0.2 mm in diameter), coated with fused alkali chlorides, was placed near the evaporating flame. A small D.C. voltage was applied to both terminals of the wire and evaporation of these metals could be accurately controlled by regulation of electric current.

The temperature was measured at various points of the ionizing flame with a fine Pt-Pt/Rh 13% thermocouple 0.1 mm in diameter.

The flame photometric method was applied to determine the distribution of free neutral atoms in the flame. A diffraction grating was used as a monochrometer and a photomultiplier tube (Hamamatsu T.V. R213) as a sensor. The spectrum intensities of lithium and sodium resonance lines in emission were measured at several points through a pipe 2 mm in inner diameter.

Distribution of charged particles in the flame was determined by the Langmuir probe method. A fine probe (Pt/Rh 13% wire 0.1 mm in diameter, (1) in Fig. 1) was inserted into the flame and a potential was applied to the probe against the ionizing jet. When the potential was varied, the

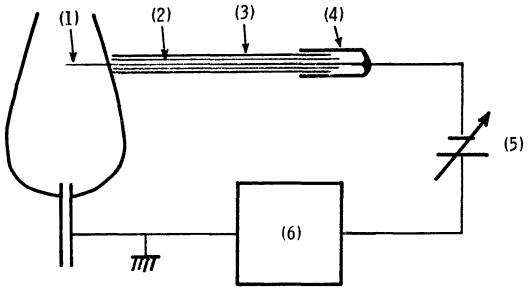


Fig. 1. Circuit for measuring probe characteristic. (1) Fine probe wire (0.1 mm D., Pt/Rh 13%); (2) Thin silica tube; (3) Copper cooling tube (1 mm I.D.); (4) Glass tube for moving the probe in a horizontal direction; (5) Voltage supplier (−3—3 V); (6) D.C. amplifier

15) T. Kinbara and H. Ikegami. *Combustion and Flame*, **1**, 199 (1957).

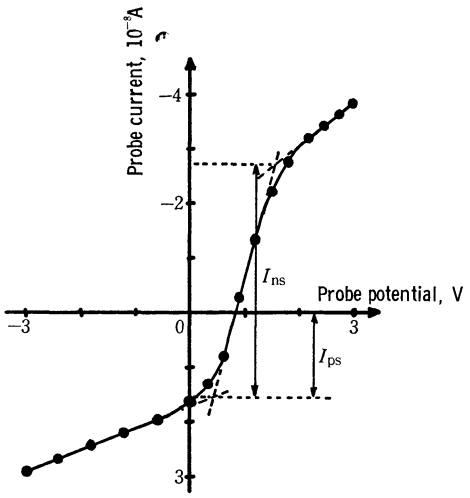


Fig. 2. Current-potential characteristic of Langmuir probe.

current-potential curve as shown in Fig. 2 was obtained. $I_{ps}$ and $I_{ns}$ are saturation currents due to only positive ions and only negative particles, respectively. The probe wire, together with its cooling tube, was mounted on the movable carriage of a cathetometer, the telescope being removed. The saturation current was measured at various points in each half of the flame. Measurements were carried out in a horizontal direction by inserting the probe in every one millimeter, and the saturation current in one position was determined by subtracting the values of two adjacent measurements.

Mobility of ions in the flame was observed by the sheath method to confirm whether the negative particles were chiefly electrons or negative ions. The diagram of the circuit used was the same as that of Kinbara.[15] A platinum wire 0.3 mm in diameter was used as an electrode. A potential difference was applied between the wire electrode and the ionizing jet. In order to observe the potential of the ionized gas, a probe of Pt/Rh 13% wire 0.1 mm in diameter was

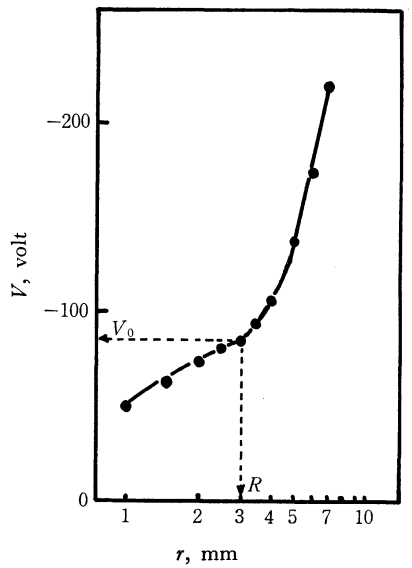


Fig. 3. Potential distribution around positively charged wire electrode.
Height of wire electrode from jet: 8 mm; $r_0$: 0.3 mm; $l$: 6 mm; Potential of jet: −600 V; $i$: $8\times10^{-8}$ A

used. The probe was covered with a thin silica tube (0.4 mm in diameter) except for 6 mm at the end. The probe, together with its silica tube holder, was mounted on the movable carriage of a cathetometer. The uncovered part of the probe was carefully adjusted to be just beneath and parallel to the wire electrode. The potential was observed by the potentiometer. By adjusting the potential $V$ of the probe with respect to the wire electrode under investigation, the probe current could be reduced to zero, at which point the probe would be at the same potential as the adjacent gas. Keeping the probe current at zero, the observed potentials of the probe were plotted as a function of ln $r$. A curve was obtained as given in Fig. 3. $r$ is the distance between the center of the wire electrode and the probe. The mobility $k_-$ for negative particles around the positive wire electrode is given by the equation.[15]

$$k_- = \frac{i[R^2 \ln(R/r_0) - 1/2(R^2 - r_0^2)]^2}{1.1 \times 10^{-12} l V_0^2 (R^2 - r_0^2)} \quad (\mathrm{cm \cdot sec^{-1}/V \cdot cm^{-1}}), \tag{1}$$

where $i$ is the total current(A) through the flame, $V_0$ the potential difference (volt) in the sheath, $R - r_0$ the sheath thickness (cm), $r_0$ the radius (cm) of the wire electrode, and $l$ the length(cm) of the wire electrode in the flame. $V_0$ and $R$ were determined from Fig. 3 and $k_-$ was calculated by Eq.(1).

It is necessary that the potential distribution is concentric with the wire electrode and uniform along its axis. Thus, measurements were carried out at 8—12 mm above the jet, where the ion distribution was relatively more homogeneous than other parts of the flame.

## Results and Discussion

The temperature distribution of the ionizing flame is given in Fig. 4, and the distribution of free sodium atoms in vertical direction in Fig. 5. Determination was carried out as follows. If spectrum intensities in any two points of the flame are $I_1$ and $I_2$, the ratio of the numbers of free atoms $N_2/N_1$ would be as follows.

$$\frac{N_2}{N_1} = \frac{I_2 V_1}{I_1 V_2} e^{E/k(1/T_2 - 1/T_1)}, \tag{2}$$

where $k$ is the Boltzmann constant, $E$ the energy of excitation (2.10 eV for sodium resonance lines), $V$ the volume of observed flame, and $T$ the mean temperature of observed flame. The ordinate of Fig. 5 is given by Eq. (2), where $N_1$ is the number of free neutral atoms in the region 0—2 mm above the jet and $N_2$ the number in the region under investigation.

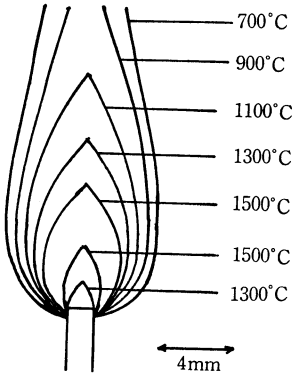


Fig. 4. Temperature distribution of ionizing flame.

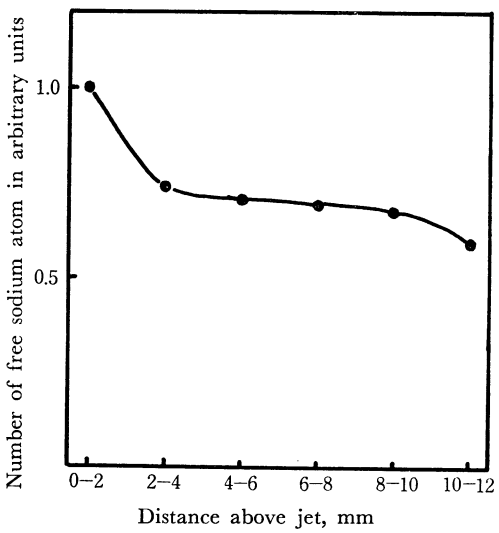


Fig. 5. Vertical distribution of free sodium atom.

The volume of inner flame 0—4 mm above the jet was subtracted from volume $V$, since it was considered that sodium atoms are not present in this part, or even if they were, the temperature of this part was too low to excite sodium atoms.

We see from Fig. 5 that free sodium atoms are mainly distributed in the lower and outer parts of the flame. In the upper part, the distribution was uniform due to the diffusion of sodium atoms.

Figure 6 shows the observed intensities of the sodium and lithium resonance lines in the emission 3—5 mm above the jet, plotted (logarithmic scale) against the reciprocal temperature. If these metals were present as free atoms, then Fig. 6 should show a straight line with slope $(-E/k)$, where $E$ is 2.10 and 1.85 eV for sodium and lithium resonance lines, respectively.

Any systematic deviation from this line would mean that a significant part of the metals was present other than as free neutral atoms, in an amount depending on

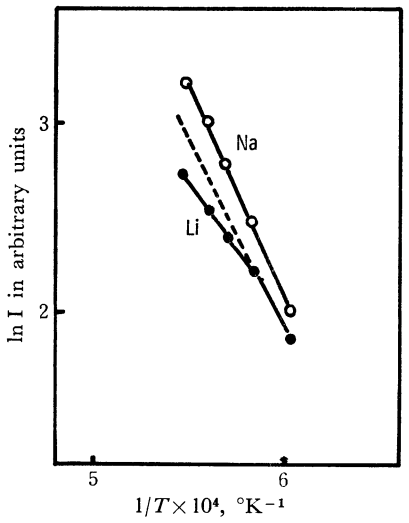


Fig. 6. Plot of ln (intensities of lithium and sodium in resonance lines) against $1/T$.
Emission intensity 3—5 mm above jet was measured. The dotted line corresponds to the theoretical slope, with the assumption that no compounds or ions are formed.

temperature. The plot for sodium showed a straight line, and $E$ agreed with the energy of resonance lines. Hence, most of the sodium is present as free atoms in this region. On the other hand, the plot for lithium deviated from the theoretical straight line with the rise in temperature. Since lithium is more difficult to ionize than sodium, the decrease of free atoms by ionization dose not cause the deviation. A reasonable source of deviation would be formation of a molecular compound. Jensen and Padley[16] considered that gaseous hydroxide was formed as

$$A + H_2O \rightleftarrows AOH + H,$$

where A is alkali metals, and they determined dissociation energies of alkali hydroxides. From their results, LiOH is a most stable compound; the stability decreases in the order CsOH, RbOH, KOH, and NaOH.

If a metal and its position in the flame are given, spectrum intensity $I$ is proportional to the number of free atoms $N$. If the number of free atoms and spectrum intensity decreased to $N'$ and $I'$ as a result of hydroxide formation:

$$\frac{[LiOH]}{[Li]} = \frac{N-N'}{N'} = \frac{I-I'}{I'}. \quad (3)$$

From the deviation in Fig. 6 and Eq. (3), it was found that [LiOH]/[Li] was 0.1—0.3 at 1500—1550°C. In the case of cesium, spectrum intensity could not be measured owing to lack of sensitivity. However, it was found from Fig. 7 that the hydroxide would be formed at 1700°C or above. Fig. 7 shows a relationship of dissociation energies of alkali hydroxides and formation temperatures of sodium, potassium, and rubidium hydroxides, determined by Jensen and Padley.[16] Only a small amount of lithium hydroxide appeared to formed. This is because the flame temperature was relatively low and alkali elements were not added as fine sprays of dilute aqueous solution.

Distributions of charged particles in the flame by the Langmuir probe method are shown in Figs. 8, 9,

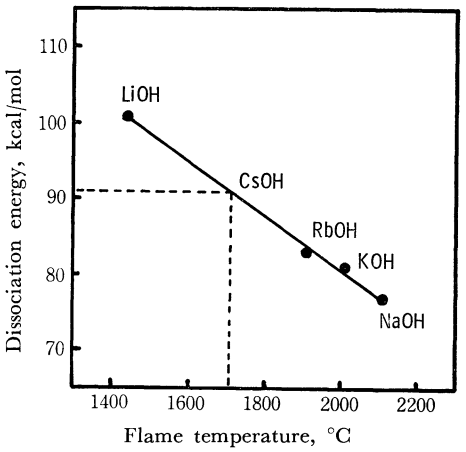


Fig. 7. Plot of dissociation energy against formation temperature of alkali hydroxides.
Temperature for the formation of LiOH was determined.

16) D. E. Jensen and P. J. Padley, *Trans. Faraday Soc.*, **62**, 2132 (1966).

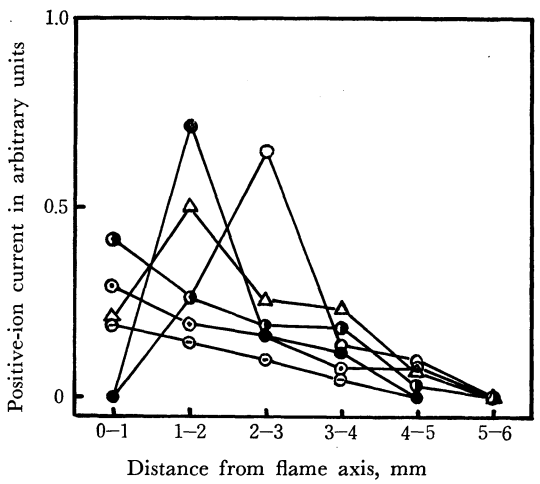


Fig. 8. Horizontal distribution of positive ion in adding sodium chloride in flame.
Distance above jet (mm): ● 1; ○ 3; △ 5; ◑ 7; ⊙ 9; ⊖ 11

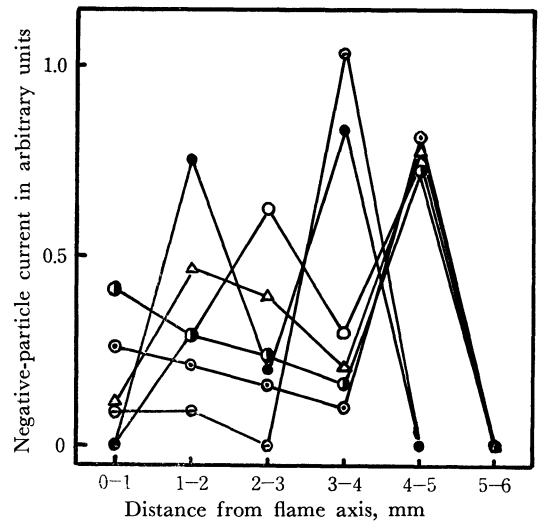


Fig. 9. Horizontal distribution of negative particles in adding sodium chloride in flame.
Distance above jet (mm): as Fig. 8.

and 10. The ordinates of these figures are represented by $I_{ps}$ or $I_{ns}$ in Fig. 2. It seemed reasonable that the positive-ion distributions have maxima in the parts of higher temperature, since alkali metals A are ionized by collisional process with flame gas molecules X, *viz.*,

$$A + X \rightleftarrows A^+ + e + X$$

and the ionization of the alkali metals is near thermal equilibrium. However, the negative-particle distributions also have larger maxima in the outer part of the flame. We see from Fig. 10 that ionization chiefly occurred in the part 0—5 mm above the jet and the negative-particle current was only about twice as large as the positive-ion current.

If negative particles were only free electrons, the negative-particle current should be much larger than the positive-ion current because of the larger mobility of free electrons. In such a small flame, however, it is possible that the higher diffusion rate of electrons allow them to diffuse out of the flame, causing a small

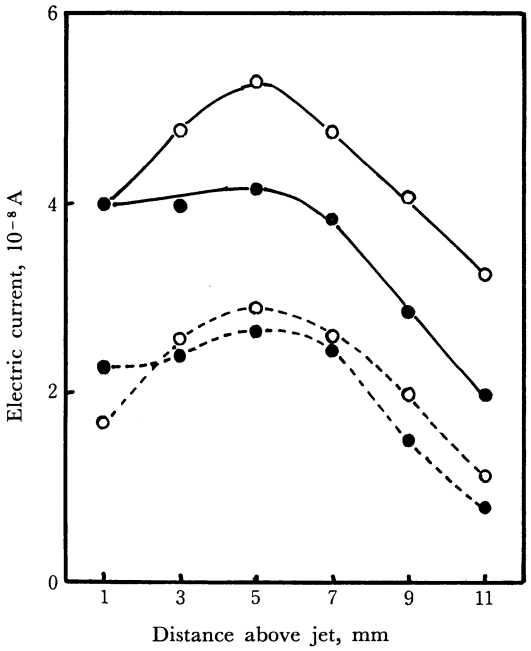


Fig. 10. Vertical distribution of positive ion and negative particles.
●: Sodium; ○: Rubidium
----: Positive ion; ——: Negative particles

negative-particle current. It appears that most negative particles are negative ions of small mobility formed by attachment of free electrons to electronegative gases such as hydroxyl radical, atomic oxygen and chlorine. However, it was not possible to distinguish electrons from negative ions by the probe method. To do this, negative-particle mobility should be measured.

Thus, the positive-ion and negative-particle mobilities were measured by the sheath method when sodium chloride was added to the flame. The plot for negative-particle mobility is shown in Fig. 3. From Eq. (1) and Fig. 3, $k_-$ was calculated to be 9 $cm \cdot sec^{-1}/V \cdot cm^{-1}$, and $k_+$ to be 0.4 $cm \cdot sec^{-1}/V \cdot cm^{-1}$. If the negative particles were free electrons, the mobility would be of an order of about $10^3$. If they were negative ions, it would be the same order as that of the positive-ion mobility. It thus seems reasonable that most of the negative particles were negative ions and a few electrons increased the mean negative-particle mobility. The negative-particle distributions in Figs. 9 and 10 showed maxima in the outer part of ionization zone. It was considered that electrons diffused to the outer surface of the flame, and negative ions were formed by attachment of electrons to the electronegative gases during the course of diffusion.